

INTERACTION OF QUANTUM DOTS WITH METALLOTHIONEIN ANALYZED BY ELECTROCHEMICAL METHODS

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INTRODUCTION

Nanomaterials with "quantum size effect" that are widely studied due to their physical and chemical properties [1], are quantum dots (QDs). The QDs with oxidative number II – IV are used in the broad range of applications including bioimagery, optoelectronic applications as fluorescent agents for in vivo imaging, and chemical sensors. Metallothionein (MT) (MT-2) as a low-molecular protein with the size of 6-7 kDa has the tertiary structure based on the presence of two domains. These domains readily form cysteine clusters to bind metal ions [2]. The main functions of MT consist in the transport of metal ions, accumulation of Zn, and detoxification of heavy metals (Cd, Hg, Pb) in organisms. Due to high affinity of MT to heavy metals, its interaction with QDs is also possible. An increased expression of MT after exposure of model organisms to Cd-based QDs has been published in works dealing with (eco)toxicity of quantum dots [3]. In another studies the biosynthesis of QDs in rats and earthworms exposed to CdCl₂ has been found [4]. In earthworms the QDs synthesis was co-localized with expression of MT. MT has been analysed by Brdicka's reaction in Brdicka's solution, which is the catalytic reaction of protein in described solution. Chemical phenomena of this reaction is based on the interaction, especially decrease of catalytic peaks [6] and formation of X and Y peaks. In this work, we aimed at detailed study of MT-QDs interaction by DPV.

ELECTROCHEMICAL DETERMINATION

The interaction of QDs with MT was also monitored electrochemically in the Brdicka electrolyte during studying catalytical signals. The mixture of 500μ M QDs and 0.6μ M MT was left to interact for the interaction time from 0 s to 6 h. Five peaks were detected (X, Y, RS2Co, Cat1, Cat2) in the obtained



voltammograms. These peaks were described according to data published in previous articles [21]. However, we were interested in X (potential of -0.90 ± 0.05 V) and Y (potential of -1.00 ± 0.05 V) peaks that appeared during the interaction [7].

Figure 1.1 shows characteristics of peaks X and Y for CuS QDs. In the time interval between 180 min and 360 min the X peak (blue graphs) increased. This increase is approximately twenty-one times, from 2.3 nA at 180 min to 49.5 nA at 360 min. In contrast, potential was shifted significantly to higher (more positive) potentials in the whole interaction range. In the case of the Y peak (red one), the peak decreased (from 64.3 to 41.4 nA) during the first minutes of the interaction (till 16 min). This effect is probably caused by the main role of MT in this interaction. After 30 min the interaction of CuS with MT caused the shift of potential to higher (more positive) values. The results of the measurement of CdS with MT are shown in Fig. 1.2. Height of the peak X increased (from -1.03 to -0.89 V).

The value of the peak X for PbS (Fig. 2.1) is the highest among all QDs (for PbS hundreds, for other QDs tens of value). The peak potential was shifted to more positive values. In the case of peak Y its height decreased up to 240 min; after this time, an increase was observed. The same course was observed for the potential. Interaction of MT with CdTe is shown in Fig. 2.2. Increase of the peak X was very rapid (forty times in 120 min). The potential was shifted significantly to positive values (from -0.99 to -0.91 V). Analogical situation was observed in the case of the peak Y, changes in its height were not so distinct (1.7x).

As it is well evident from all obtained results, the peaks X and Y increased with the prolonged time of interaction; on the other hand, Cat2 peak (data are not presented) decreased. The Cat2 peak corresponds to the presence of –SH moieties; MT interacts with QDs via these sulfhydryl moieties within its structure. During the interaction between MT and QDs, free -SH groups in MT are probably saturated by QDs and this effect causes observed increase of height of the X and Y peaks as a proof of metal reduction in the complex MT-QD [8]. However the explanation of the interaction is still unknown and it is the subject of another experiment.

Figure 1. Interaction of MT with QDs. (1.1) Interaction of CuS with MT in time interval from 0s to 6h. Dependence of peak height and peak position on interaction time for peak X (-0.94 V) and peak Y (-0.99 V). (1.2) Interaction of CdS with MT in time interval from 0s to 6h. Dependence of peak height and peak position on interaction time for peak X (-0.97 V) and peak Y (-1.01 V).



Figure 2. Interaction of MT with QDs. (2.1) Interaction of PbS with MT in time interval from 0s to 6h. Dependence

CONCLUSION



Complexes formed during interaction of QDs with MT were studied in our work by Brdicka catalytic reaction, which providing new peaks X and Y associated with MT-QD complexes. The experimental results bring new information about interaction of different types of QDs with MT. Our study becomes the basis for further research, because the future use of QDs will always be associated with the question of their possible binding to metalloproteins that are capable to bind readily heavy metals.

of peak height and peak position on interaction time for peak X (-0.95 V) and peak Y (-1.02 V). (2.2) Interaction of CdTe with MT in time interval from 0s to 6h. Dependence of peak height and peak position on interaction time for peak X (-0.95 V) and peak Y (-1.00 V).

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